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THE COMPLEXATION OF CYCLIC POLYETHERS AND A SERIES OF EQUATIONS FOR DETERMINATION OF EQUILIBRIUM CONSTANTS

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ABSTRACT

An outstanding and compact formalism was established to estimate the equilibrium constants K_e of essential ligands with well-known structures like crown ethers, or unknown complexing stoichiometries The application of the general formula $1/K_e[L_0]^{m+n-1} = (1/P_L - 1)(1 - P_L)^{m+n-1}$ is described by the computer-simulated plots, where m/n is the complexing ligand/cation ratio, P_L is the mole fraction of the complexed ligand and $[L_0]$ is the initial ligand concentration of the complex solution

INTRODUCTION

Before we start to discuss the measurement of the cation binding tendency of cyclic polyethers and their ether–ester analogues, it is worth mentioning the specific cation solvation mechanism of such molecules, which consist of both hydrophilic ether dipoles and hydrophobic methylene exteriors Excellent reviews have appeared in the literature [1–6]

Despite recent developments in solution chemistry, there are several considerations which sometimes cause undesirable contradictions between the results of some investigators studying similar structures or solute–solvent systems

We believe that the crown ether chemist should take into account the following factors (a) the aggregation of the ions and the ion pairs, (b) the complex-cation and counterion mobility, even in water, (c) the rough estimations of the values of the governing thermodynamic factors such as activity coefficients, (d) the inability of equations to determine the analytical and thermodynamic parameters, (e) the limited instrumental methods for the wide range of reactive centres, (f) the complex role of the mother solvent and the interaction among ligand molecules and the solvent media, (g) the difficulty of computations regarding the above-mentioned intermediates due to particular thermal changes

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However, the cyclic ethers of oligomers of ethylene oxide and similar structures eliminate some of these considerations owing to the uniform structures of the ligands. In addition, there is no need to criticize the common analytical methods as this has already been carried out, [7,8].

The most interesting point may be the least studied part of the cation binding behaviour of cyclic polyethers, i.e. the formation of the polyether-complexed ion pairs in equilibrium with the crown-separated ion pairs as is characterized by the ion pairs theory [9]. The existence of thermodynamically distinct species depends on the distance between the ions and counterions. In water solutions the formation of the crown-complexed ion pairs is particularly complicated owing to incomplete dissolution of the cation. However, the electric field and the interactions between the ions are normally under the control of the intrinsic polarity of the macrocyclic cavity or vice versa.

It is important to recognize that the dilution of the complex may cause free ion formation, whereas increased complex concentrations will lead to the aggregation of ion pairs. This should be examined with extreme care by the analyst so that he can work in as wide a concentration range as possible [4,5,10].

The equilibrium constant of a host–guest complex is known to be influenced by macrocyclic ligand conformation, ligand thickness, incomplete encapsulation, binding site, ligand dimensions and number of ligand molecules in a complexed ligand structure. On the other hand, for non-chelating ligand solvation or coordination, the use of any method and equation system would carry its difficulties owing to the random structure of the primary and secondary solvation spheres.

Regarding the arguments on the equilibrium constants, of prime importance is the stoichiometry of complexation and the actual ratio of the concentrations of the cation and ligand in a solution. When applied more or less in a classical manner the equilibrium or stability constants are not more than a mathematical logic compared with the discussion of the limitations of the use of activity coefficients (eqn. (1)) [3,11a,12a]. In general, if the role of the activity coefficient f_a is omitted in the estimation of the values of the constants K_e, then eqn. (3) is tried.

$$mA^+ + nL \rightleftharpoons A_m^+L_n \tag{1}$$

$$K_c = f_c[A_m^+L_n]/f_a[A^+]^m[L]^n \tag{2}$$

The actual complexing stoichiometry involved in the solution sometimes differs from what is predicted. Both the possibility of the formation of ion aggregates or triple ions in poorly-dissociating media and the various ligand-to-cation ratios of the complexes effect the equilibrium constants in polar media (Fig. 1).

However, the K_e values are obtained from a graph of concentration versus mole fraction of complexed ligand for different stoichiometries, where

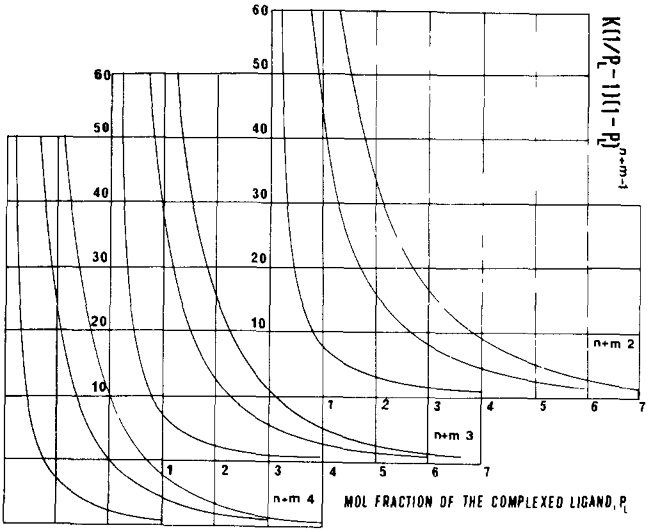

Fig 1 Plots of ligand mole fraction P_L versus complexation degree $(1/P_L - 1)(1 - P_L)^{m+n-1}$ for different stoichiometries and different equilibrium constants K_e

$1/K_e[L_0] = (1/P_L - 1)(1 - P_L)^{m+n-1}$ and Fig 1 is obtained Although this is a very well-known fact, it clearly displays the extremely narrow experimental error range to be taken into account for any equilibrium constant determination In many cases, extreme care is required to distinguish the

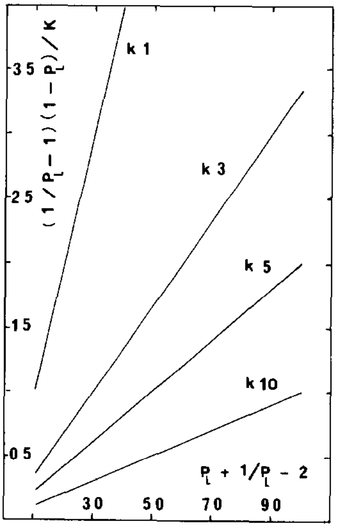

Fig 2 Plots of complexation degree $(1/P_L - 1)(1 - P_L)$ versus $P_L + 1/P_L - 2$ for 1 1 ratio of cation/ligand Inverse ligand concentration is obtained from $P_L + 1/P_L - 2 = 1/[L_0]$ K_e values indicated on the graphs K_e values are given as integers

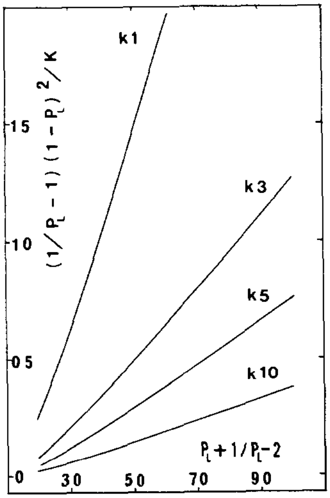

Fig 3 Plots of complexation degree $(1/P_{\mathrm{L}}-1)(1-P_{\mathrm{L}})^2$ versus $P_{\mathrm{L}}+1/P_{\mathrm{L}}-2$ for 1 2 ratio of cation/ligand Inverse ligand concentration is obtained from $P_{\mathrm{L}}+1/P_{\mathrm{L}}-2=1/[\mathrm{L}_0]$ K_{e} values indicated on the graphs K_{e} values are given as integers

drops in concentration as a result of the complexing order, unless large differences exist in association degree or association constants (Fig 1)

Accordingly relationships were suggested, and were plotted to represent some possible mole fraction values against the inverse degree of concentration of cation or ligand (Figs 2–4)

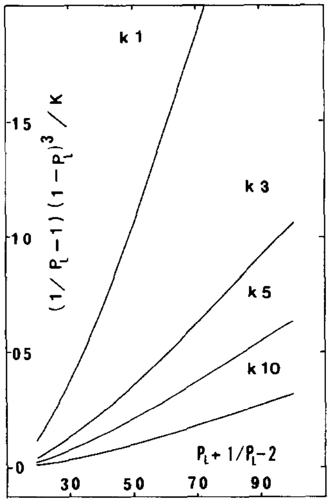

Fig 4 Plots of complexation degree $(1/P_{\mathrm{L}}-1)(1-P_{\mathrm{L}})^3$ versus $P_{\mathrm{L}}+1/P_{\mathrm{L}}-2$ for 1 3 ratio of cation/ligand Inverse ligand concentration is obtained from $P_{\mathrm{L}}+1/P_{\mathrm{L}}-2=1/[\mathrm{L}_0]$ K_{e} values indicated on the graphs K_{e} values are given as integers

RESULTS AND DISCUSSION

To calculate the equilibrium constants, K_e, the variation in the mole fraction of the ligand–cation system was considered for the various stoichiometries

$$K_e = [A^+_m L_n]/[A^+]^m [L]^n \tag{3}$$

If $P_A = P_L$ is considered experimentally by taking identical cation and ligand concentrations, i e $[L_0] = [A^+_0]$, then the following sets of relationships are obtained (Fig. 2)

$$P_A = [A^+_m L_n]/[A^+_0]\, P_L = [A^+_m L_n]/[L_0] \tag{4}$$

$$K_e = P_L[L_0]/\{[L_0] - [A^+_m L_n]\}\{[A^+_0] - [A^+_m L_n]\} \tag{5}$$

$$K_e = P_L/[L_0](1 - P_L)^2 \tag{6}$$

$$1/K_e[L_0] + 2 = P_L + 1/P_L \tag{7}$$

However, for the different stoichiometries of complexation the following equations can be derived· for 1 · 2 and 1 3 ratios eqns (8) and (9) are obtained, where $[L_0] = [A^+_0]$ is retained experimentally

$$1/K_e[L_0]^2 = (1/P_L - 1)(1 - P_L)^2 \tag{8}$$

$$1/K_e[L_0]^3 = (1/P_L - 1)(1 - P_L)^3 \tag{9}$$

As can be seen, the simulated mole fraction values were varied in a certain concentration range for a desired K_e value (Table 1) Accordingly,

TABLE 1

The numerical values of an equilibrium for the 1 1, 1 2 and 1 3 ratio of cation to ligand stoichiometry (see also Figs 2–4) [a]

$1/[L_0]$	(P)	$(P+1/P-2)/K$ [b]	$(1/P-1)(1-P)^2/K$ [c]	$(1/P-1)(1-P)^3/K$ [d]
1 000	0 3820	0 2000	0 1236	0 0764
2 000	0 2679	0 4000	0 2928	0 2144
3 000	0 2087	0 6000	0 4748	0 3757
4 000	0 1716	0 8000	0 6627	0 5490
5 000	0 1459	1 0000	0 8541	0 7295
6 000	0 1270	1 2000	1 0476	0 9145
7 000	0 1125	1 4000	1 2425	1 1027
8 000	0 1010	1 6000	1 4384	1 2931

[a] The simplified computer program in BASIC for such applications is available from the author [b] $K_e = 5\ 00$ for 1 1 ratio of complexing (Fig 2) [c] $K_e = 5\ 29$ for 1 2 ratio of complexing (Fig 3) [d] $K_e = 5\ 69$ for 1 3 ratio of complexing (Fig 4)

in the case of a common ligand to cation ratio m/n of complex formation a general equation can be given (eqn (10)) where $[L_0] = [A_0^+]$

$$1/K_e[L_0]^{m+n-1} = (1/P_L - 1)(1 - P_L)^{m+n-1} \tag{10}$$

Regarding the complexes with unknown stoichiometry, one can obtain both the equilibrium constant K_e and the total stoichiometry $n + m$ by use of the relationship

$$(1 - m - n) \log K_e + \log[L_0] = (m + n - 1) \log(1 - P_L) + \log(1/P_L - 1) \tag{11}$$

Thus the use of the above series of equations enables the analyst to work on any instrument It is usual to measure the mole fractions of the complexed cation or ligand with any method and then to apply the above equations, as reported from our laboratory recently [11b,d,e,12f]

Thus, the deviations from predicted values reflect the actual mechanism and stoichiometry, since the deflections represent changes in the route of complexation we run the entire concentration range which is likely to yield useful results [11e,12f]

For selected K_e values, the mole fractions of complexed ligand were calculated, and plotted with a computer throughout the probable concentration ranges

It is therefore useful to try a program in which the relationship between the initial concentration of the ligand or cation and the mole fraction of the complexed ligand is established The dependence of ligand concentrations on the mole fractions of the complexed ligand or the cation are plotted in Fig 1 However, further plots of eqns (7)–(9) clearly display the dependence of the equilibrium constant K_e on the mole fraction, governed by the total complexing stoichiometry $m + n$ (Figs 2–4)

This method examines both the theoretical and experimental facts, as well as proving the experimental results with the use of graphs like Figs 2–4 Producing such a program to examine the results is a simple task

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